AN INFRARED STUDY OF HALOGEN
SUBSTITUTED ETHERS

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By

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CHAPTER I

INTRODUCTION

Up to the present time little has been done toward elucidating
the infrared spectra of the ethers as a class of organic compounds.
Crawford and Joyce (1) have studied dimethyl ether from a theoretical
standpoint, and Herzberg (2) mentions the work of several investigators
of this molecule. Many workers (3-7) have included ethers among
those compounds studied in an effort to find absorption bands character-
istic of functional groups contained in the molecules. These studies
reveal that the spectra of unsubstituted ethers contain an absorption
band at approximately 9.00 microns which is associated with the C-O
stretching vibration. Although Batuev, Prilezhaeva and Shostakovskii
(8) have studied the Raman spectra of vinyl alkyl ethers, and Szobel (9)
has studied the near infrared spectra of dibutyl and dimethyl ethers and
their oxonium compounds, no attempt has been made to determine how
the frequency of this characteristic absorption depends on the structure
of the ether, or how substitution of the ether with various halogens af-
fects this absorption.

Recently ethers containing fluorine and chlorine have been pre-
pared (10-15) which present particularly confusing spectra since the
characteristic frequencies of C-F bands occur in the same region of
the spectrum as that of the ether link. The spectra of many of these

compounds have been determined (11-12), but no earnest effort has been made to explain the absorption except in the most general way. Indeed, some assignments (12) have been made for the C-O absorption in these ethers which, in the light of the present study, appear erroneous.

The intent of the present work is to examine the spectra of two series of these halogenated ethers and a single member of a third series. The series to be considered are the difluoro-dichloro-ethyl alkyl ethers ($ROCF_2CHCl_2$), the trifluoro-chloro-ethyl alkyl ethers ($ROCF_2CHFCl$) and the tetrafluoro-ethyl alkyl ethers ($ROCF_2CHF_2$). In this study the alkyl groups used include methyl, ethyl, n-propyl and isopropyl in the first two series but only ethyl in the remaining series. An attempt has been made to identify the absorptions associated with the C-O stretching vibration as well as those arising from the C-F bonds in the molecule. The effect of a change in halogen substitution on these absorptions has been investigated as well as the effect of a change in the aklyl group.

At this point a brief discussion of the basic theory of infrared absorption spectra and absorption spectra in general seems in order. A detailed discussion is, of course, out of the question, but may be found in Herzberg's work "Infrared and Raman Spectra of Polyatomic Molecules" (2). The present discussion is designed to include a few of the fundamental ideas and to make note of a few of the common difficulties encountered in a rigorous approach.

If one considers a molecule as a group of atoms tied together

by a system of forces such that each atom affects every other atom in the molecule, it then appears that all the vibrations of the molecule may be described by the superposition, with the proper amplitude, of a set of characteristic vibrations. These vibrations are determined by the magnitude of the forces between the atoms and their arrangement in space. Furthermore, if one assumes that each vibration is excited by only a single quantum of energy, the resulting frequencies are the fundamental frequencies of the system. If, in addition, one expresses these vibrations in terms of a set of coordinates relating each nucleus in the molecule to a fixed position in space, the vibrations are called normal vibrations. Since each nucleus contributes three degrees of freedom to the system, there are, for a molecule containing N nuclei, 3N normal vibrations. However, some of these vibrations correspond to translation and rotation of the molecule in space and, consequently, have no vibrational frequency. These are called non-genuine vibrations and are five and six in number for linear and non-linear molecules respectively. The number of genuine normal vibrations for a molecule then becomes 3N-5 or 3N-6 depending on whether the molecule in question is linear or non-linear.

If only small displacements of nuclei from their equilibrium positions are considered, the vibrations are harmonic and may be treated by means of the well known mathematical tools developed for the harmonic oscillator. In general, the frequency of oscillation of a

given atom may be expressed as a linear function of the displacements
in the x, y and z directions, the mass of the atom and the appropriate
force constants. When such an expression is written for each vibrating
nucleus, a secular determinant may be formed which, when solved,
uniquely determines the frequencies of all the normal vibrations. As
long as anharmonicity is neglected, the method is applicable to the
most complicated systems, although it becomes somewhat laborious
as the number of atoms in the system increases. In actual practice,
however, harmonic systems are seldom encountered, and quadratic
or higher terms must be added to the equations composing the secular
determinant. This fact further increases the difficulty in calculating
the normal vibrational frequencies, and makes it quite impossible for
more complicated molecules.

In the case of the harmonic oscillator, it can be shown that
only the fundamental vibrations appear; however, where anharmonicity
is present, overtone and combination vibrations can and do appear.
Overtone vibrations arise when a particular vibration is excited by
more than one quantum, and combination bands are the result of two
vibrations, which may be either fundamentals or overtones, combining
to give rise to a different vibration. The presence of these overtone
and combination vibrations produces further complication. When dif-
ferent excitation levels of two characteristic vibrations happen to fall
close together, both of them are perturbed, are moved away from their

expected frequencies, and are to some extent mixed. This phenomenon is termed accidental degeneracy or "Fermi Resonance". It must not, however, be confused with the degeneracy which occurs when the secular determinant mentioned above happens to have two or more roots which are identical. This latter type of degeneracy arises from the symmetry of the molecule, and can be predicted from considerations involving this symmetry.

It has been found that the operations which may be performed on a particular molecule such as rotation about an axis, reflection in a plane, or inversion through a point, when taken together, form a mathematical group. That is to say, performing any two allowed operations in succession results in the same spatial orientation of the molecule as would result from performing some other, single, allowed operation. It is further known that there exist only a limited number of such groups into which all molecules may be classified. These are referred to as point groups, and the point group to which a molecule belongs is determined by the type and number of operations allowed by its symmetry.

The separation of molecules into these point groups makes it possible to classify the various normal vibrations into species. The species to which a particular vibration belongs depends on the behavior of that vibration with respect to the symmetry elements present. For example, if the spatial orientation of a vibration remains unchanged after a symmetry operation has been performed on it, it is said to be

symmetric with respect to that operation; if the vibration changes nothing
but its sign, it is said to be anti-symmetric. It is, of course, possible
for vibrations, in molecules with several elements of symmetry, to be
symmetric to one symmetry element but not to the others. A vibration
may also be symmetric with respect to more than one of the symmetry
operations allowed and may, in fact, be symmetric to all of the allowed
symmetry operations. In this case the vibration is called "totally sym-
metric". Although non-degenerate vibrations may behave in only two
ways under a given symmetry operation (that is, they may change in
sign or remain unchanged), degenerate vibrations may change by more
than just the sign. For this reason they cannot be classed as symmetric
or anti-symmetric.

When a molecule in its ground state absorbs radiant energy,
it may do so only in discrete amounts, each amount (quantum) absorbed
serving to raise it to a higher energy level. As mentioned before, each
fundamental vibration corresponds to absorption by the molecule of one
quantum of energy. The rotation of a molecule in space is similarly
quantized, and a molecule possesses rotational fundamentals as well.
Since the difference between the energy of rotational levels is always
smaller than between the energy of vibrational levels, the quanta
exciting rotational transitions fall in a different region of the electro-
magnetic spectrum from those exciting vibrational changes. It has been
found that the infrared region of the spectrum contains quanta with the

necessary energy to excite both types of transition; however, the vibrational quanta occur largely in the region between one and twenty-five microns while the rotational quanta occur at longer wave lengths.

In order to determine the vibrational or rotational energy of a molecule experimentally, it is, of course, necessary to rely on radiation which has been absorbed by the molecule. Infrared absorption spectra arise from direct absorption of radiation by the molecule; however, every mode of vibration of the molecule is not always represented by a corresponding absorption in the spectrum, since it is required that a vibration be accompanied by a change of dipole moment if radiation is to interact with it and be absorbed. It should also be noted that, although energy is absorbed in discrete quanta, the absorption spectrum generally consists of bands rather than definite lines. This is primarily due to the fact that each vibration level may possess numerous sub-levels associated with different rotation states. This makes possible many different, discrete changes which are very close together and ordinarily not resolved.

Raman spectra offer another method of determining vibrational and rotational energies of molecules. This type of spectrum is obtained by exciting the molecule with appropriate radiation of known frequency, then determining the frequency of the radiation which it re-emits. The difference between the energy of the exciting quanta and the emitted quanta correspond to the energy of vibration or rotation. In this case the

vibrations or rotations need not be accompanied by a change in dipole moment, but must be associated with a change in polarizability of the molecule. It is, of course, possible that the conditions necessary for Raman absorption and infrared absorption may be met simultaneously so that an absorption band representing a particular transition is found in both types of spectrum.

The intensity with which a given vibration absorbs energy depends on several factors. In the case of the infrared spectrum, the magnitude of the change in dipole governs the intensity of absorption. If this change is small, the absorption is likely to be weak. It also happens that certain groupings of atoms often have a characteristic frequency which is changed only slightly as the environment of the group is changed. In this case the intensity of absorption due to such a group is roughly proportional to the number of these groups present. The third factor governing the intensity of absorption is the purely quanti-tative one as expressed by the Bouger-Beers law. This law introduces a proportionality between the intensity of absorption and the path length and concentration.

If the ethers with which this study is concerned are considered in the light of the preceding discussion, it can be deduced that the methyl, ethyl and propyl ethers should have thirty, thirty-nine and forty-eight normal vibrations respectively. The $ROCF_2CHFCl$ ethers possess no element of symmetry except the identity operation. That is to say, the

only operation which changes the molecule into itself is rotation through 360 degrees about an axis through the molecule. According to Herzberg (2), these ethers then fall into the point group C_1 and have only one species of vibration which is designated A. All these vibrations are totally symmetric with respect to the identity operation.

The symmetry of the compounds $ROCF_2CHCl_2$ and the compound $CH_3CH_2OCF_2CHF_2$ is doubtful. There are, however, only two possibilities. If the methyl, the methylene, the $CHCl_2$ or the CHF_2 group are oriented in an unsymmetrical way with the plane of the C-O-C structure, the molecules possess no symmetry element other than the identity operation and fall into the point group to which the $ROCF_2CHFCl$ type ethers belong. However, if the molecules are in their most symmetrical configuration, they then have the C-O-C plane as a plane of symmetry and belong to the point group C_s. If this is the case, the vibrations can then be divided into two species; those which are symmetric to reflection through the plane of symmetry, called A' vibrations, and those which are anti-symmetric to this operation, called A" vibrations. It should be noted that molecules belonging to either C_s or C_1 can have no degenerate vibrations unless accidentally so. Using the formulas given by Herzberg (2) for calculating the number of vibrations in each species, it is found that the methyl ethers have eighteen A' vibrations and twelve A" vibrations, the ethyl ethers have twenty-three A' vibrations and sixteen A" vibrations, the n-propyl ethers have twenty-eight A'

vibrations and twenty A" vibrations, the isopropyl ethers have twenty-seven A' vibrations and twenty-one A" vibrations.

The above considerations make it clear that a formal treatment of the ethers which have been studied is almost impossible. Much valuable information of an empirical nature can be derived from a less rigorous approach. This is particularly true with regard to correlations of elements and groups with the spectra of the compounds containing them.

CHAPTER II

EXPERIMENTAL TECHNIQUES

Preparation of Compounds

The ethers used in this study were prepared by methods which have been described in the literature. The $ROCF_2CHCl_2$ compounds have been prepared by Park and others (12) as well as by Tarrant and Young (15) by adding the appropriate alcohol across the double bond in $CF_2=CCl_2$. This was accomplished by bubbling the olefin into the alcohol, which was saturated with sodium or potassium alkoxide. The base catalyzed reaction which takes place proceeds according to the equation:

$$ROH + CF_2=CCl_2 \ ----> \ ROCF_2CHCl_2$$

The resulting mixture, containing the desired ether and unreacted alcohol, was then poured into several times its own volume of cold water. The lower, ether-rich layer was then separated and washed several times with water to remove residual traces of alcohol. This layer was then dried over calcium chloride and distilled using a packed fractionating column. The methyl, ethyl and n-propyl ethers were distilled under 760 millimeters pressure and boiled at 105, 121 and 140 degrees centigrade respectively. This compares with boiling points of 104, 120 and 136.5 degrees centigrade determined under the same pressure by Park and others (12). The refractive indices of these ethers were measured

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at 25 degrees centigrade with respect to the D line of sodium and were found to be 1.3862, 1.3892 and 1.3972 for the methyl, ethyl and n-propyl ethers respectively. They compare with the values, measured under the same conditions, given by Park and others (12) of 1.3864, 1.3895 and 1.3968 for the respective ethers.

The isopropyl ether could not be distilled at atmospheric pressure without decomposition; therefore, a distillation at reduced pressure was undertaken. The material was found to boil between 34 and 37 degrees centigrade at a pressure of 10 millimeters. The refractive index of the isopropyl ether, measured in the same manner as those of the other ethers, was found to be 1.3895. The refractive index reported by Tarrant and Brown (13) for this ether is 1.3897.

The $ROCF_2CHFCl$ compounds were prepared in precisely the same manner except that the olefin used was $CF_2=CFCl$ instead of $CF_2=CCl_2$. This preparation has been described in detail by Park and others (10) and proceeds according to the equation:

$$ROH + CF_2=CFCl \longrightarrow ROCF_2CHFCl.$$

The dried ethers resulting from this reaction were distilled under a pressure of 760 millimeters using the same column described previously. The methyl, ethyl, n-propyl and isopropyl ethers boiled, under these conditions, at 70.5, 88.0, 109 and 100 degrees centigrade respectively. Park and others (10) reported boiling points, measured

under 630 millimeters pressure, of 64.4 degrees for the methyl ether, 82.0 degrees for the ethyl ether, 102.3 degrees for the n-propyl ether and 94.0 degrees for the isopropyl ether. If Craft's rule,

$$\Delta T_b = 0.00012 T_b (P_2 - P_1),$$ is used to correct these values to 760 millimeters pressure, the corrected boiling points are 69.7 degrees for the methyl ether, 87.5 degrees for the ethyl ether, 108.2 degrees for the n-propyl ether and 99.7 degrees for the isopropyl ether.

The refractive indices for these ethers were reported by Park and others (10) to be 1.3338, 1.3479, 1.3575 and 1.3521 for the methyl, ethyl, n-propyl and isopropyl ethers respectively. These values were obtained at a temperature of 20 degrees centigrade using the D line of sodium. The refractive indices of the ethers prepared in this study were determined at 25 degrees centigrade, using the D line of sodium, and were found to be 1.3316, 1.3454, 1.3550 and 1.3499 for the methyl, ethyl, n-propyl and isopropyl ethers respectively.

The compound $CH_3CH_2OCF_2CHF_2$ was obtained from Dr. Paul Tarrant of these laboratories. This substance was prepared using a method reported by Tarrant and Young (14) in which CHF_2CF_2Cl (Freon 124-A), potassium hydroxide and ethanol were allowed to react in a rocking autoclave. The two successive reactions which occur are given by the following equations:

$$CHF_2CF_2Cl + KOH \xrightarrow{ROH} CF_2=CF_2 + KCl + H_2O$$

$$CF_2=CF_2 + CH_3CH_2OH \xrightarrow{KOH} CH_3CH_2OCF_2CHF_2 .$$
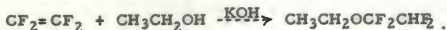
The sample of ether obtained from Dr. Tarrant was dried and distilled under a pressure of 760 millimeters and found to boil at 57.0 degrees centigrade. Park and others (11), who prepared this ether by direct addition of ethanol to $CF_2=CF_2$, reported a boiling point of 50.7 degrees centigrade obtained under a pressure of 621.7 millimeters. When Craft's rule is used to correct this value to 760 millimeters pressure, a value of 55.5 degrees centigrade is obtained.

The α-chloro-ethyl ethyl ether used in this study was prepared using a method described by Sherril and Walter (16) in which an equimolar mixture of absolute alcohol and pure-acetaldehyde was treated with anhydrous hydrogen chloride at zero degrees centigrade. After an hour the mixture separated into two layers. The top layer was dried over calcium chloride and then distilled at reduced pressure. The fraction boiling between 27 and 35 degrees centigrade at 150 millimeters pressure was retained and redistilled at 760 millimeters pressure. The ether prepared in this manner boiled between 93 and 94 degrees centigrade.

The β-chloro-ethyl ethyl ether used was prepared according to a method given by Hurd and Fowler (17). One mole of ethyl cellosolve (β-ethoxy-ethanol) was mixed with one-half mole of dry pyridine, and this mixture was cooled to zero degrees centigrade. A mixture of

100 grams of thionyl chloride in 80 cubic centimeters of chloroform was added slowly, and the mixture was then warmed gradually to 100 degrees centigrade. The warming process was accompanied by vigorous evolution of sulfur dioxide which continued for about four hours. The residue was washed with dilute hydrochloric acid, then with sodium carbonate solution, then, finally, with water. The ether was dried over calcium chloride and distilled under a pressure of 760 millimeters. The fraction boiling at 106 degrees centigrade was retained.

The pentachloro-ethyl ethyl ether used was also obtained from Dr. Paul Tarrant. The fractionated product boiled at 63 degrees centigrade under a pressure of 4 millimeters.

The methyl ethyl ether, ethyl n-propyl ether and ethyl isopropyl ether, the spectra of which were used for purposes of comparison, were prepared by straight-forward Williamson syntheses. They were then distilled, and fractions retained which possessed the well-known boiling points of these compounds.

Samples of diethyl ether, dibutyl ether, diisopropyl ether, dihexyl ether and di-2-ethyl-n-hexyl ether were obtained from stock. The samples of methanol, ethanol and n-propanol used were also obtained from stock.

Determination of Spectra

The infrared spectra of the compounds discussed above were determined immediately after purification using a Perkin Elmer Model 21 infrared recording spectrometer equipped with sodium chloride optics. The range of this instrument extends from two to fifteen microns; however, for the purposes of this study the bands of greatest interest fall between 3.00 and 4.00 microns and between 6.50 and 10.00 microns; consequently only these portions of the spectra have been shown in the accompanying figures.

The spectra of all the compounds studied were determined from their carbon tetrachloride solutions. The procedure was adopted because the high vapor pressures and low viscosities of some of the ethers made sampling of the pure liquids difficult. A preliminary study, however, indicated that there was no difference between the spectra of the compounds in solution and the spectra of the pure liquids. It was observed, in fact, that the spectra of the pure liquids did not differ appreciably from their spectra in carbon tetrachloride at a concentration as low as 0.006 molar. Since this was found to be the case, it was possible to choose a convenient concentration and to determine the spectra of all the compounds studied at this concentration.

The factor governing the choice of concentration was, of course, the intensity of absorption obtained for a given cell length. It was found desirable to choose a concentration such that the strongest bands absorbed

about ninety per cent of the incident radiation when the solutions were placed in cells about 0.1 millimeter thick. These concentrations made the weaker bands sufficiently absorbing to be easily distinguished from instrumental noise, and allowed the stronger bands to be observed with maximum resolution. Experiment showed that a concentration of about 0.2 molar met these conditions satisfactorily. Since only approximate concentrations were necessary for this work, the volume required for this concentration was computed from the approximate densities and known molecular weights of the ethers. This quantity was pipetted into a 25 milliliter volumetric flask from a 1 milliliter serological pipette and diluted to the mark with Merck reagent grade carbon tetrachloride.

The spectrometer used for these determinations was a double beam instrument in which the optical path containing the sample is electronically compared with an identical reference beam. A signal arising from the difference in the two beams is suitably amplified and fed to a drum-type, pen recorder. Comparison of the two beams in this fashion automatically compensates for absorbing bands of water and carbon dioxide which are always present in the atmosphere, and, in addition, provides a means of compensating for the absorption of the solvent in which the material is dissolved. In order to achieve the latter, matched cells of sodium chloride are used, one of which contains the solution to be investigated, the other containing only the solvent. The cell containing the solution is placed in the sample beam and is balanced

by placing the cell containing only solvent in the reference beam. If the cells are closely matched, if the solvent has been chosen correctly, and if the concentration of the solute is not too high, the resulting spectrum is essentially that of the solute.

The pen trace shown by Curve I, Figure 1 was obtained by operating the instrument with both paths empty. This curve indicates the degree to which atmospheric absorbers have been compensated as well as the magnitude of the electronic noise inherent in the amplifying system. The pen trace shown by Curve II, Figure 1 was obtained when the cells used in this study, two carefully matched cells approximately 0.1 millimeter in length, were both filled with carbon tetrachloride and placed in the sample and reference beams of the insturment. Examination of these two curves shows that compensation for atmospheric absorbers and solvent was excellent, and that the noise level for the instrument is not very high. The prism drive in this instrument is calibrated in microns; therefore, the position of the absorption bands, listed in the following parts of this study, is read directly from the chart in microns to the nearest 0.02 micron.

Figures 2 through 13 show the spectra of the substituted ethers studied. The spectra, as they appear, represent exactly the trace produced by the instrument used when it is operated at a scanning speed of approximately 0.5 micron per minute with a wave length scale of 1 inch per micron.

| 3.00 | 4.00 | 6.00 | 7.00 | 8.00 | 9.00 | 10.00 |

MICRONS

CURVE I : NOISE LEVEL

| 3.00 | 4.00 | 6.00 | 7.00 | 8.00 | 9.00 | 10.00 |

MICRONS

CURVE II: SOLVENT COMPENSATION
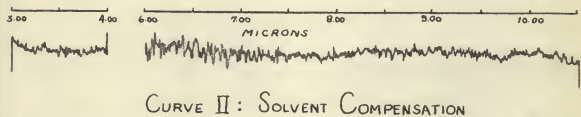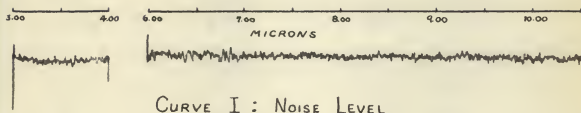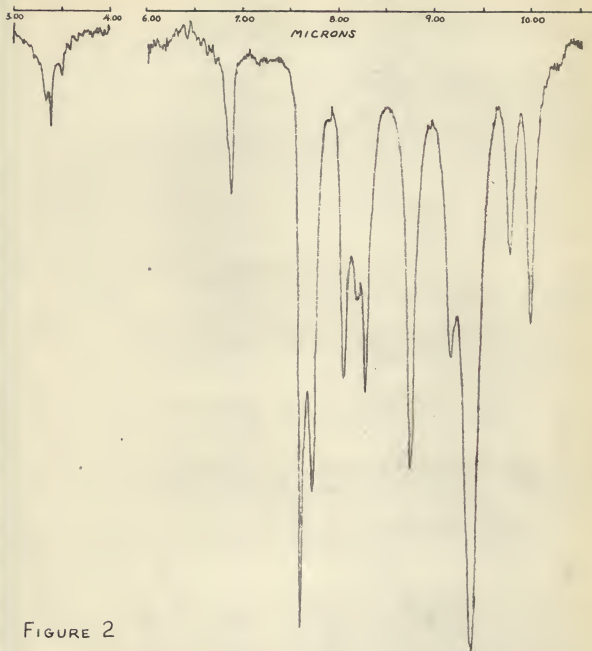
FIGURE 1

FIGURE 2

SPECTRUM OF $CH_3OCF_2CHCl_2$
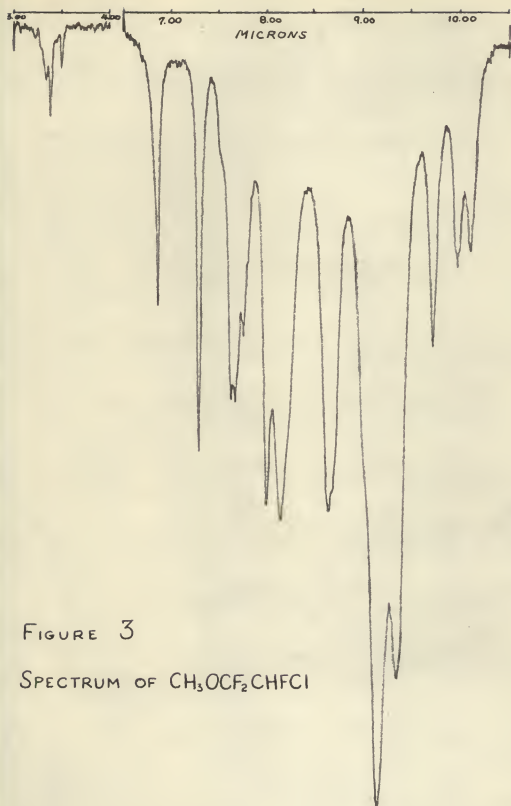
FIGURE 3

SPECTRUM OF CH₃OCF₂CHFCl
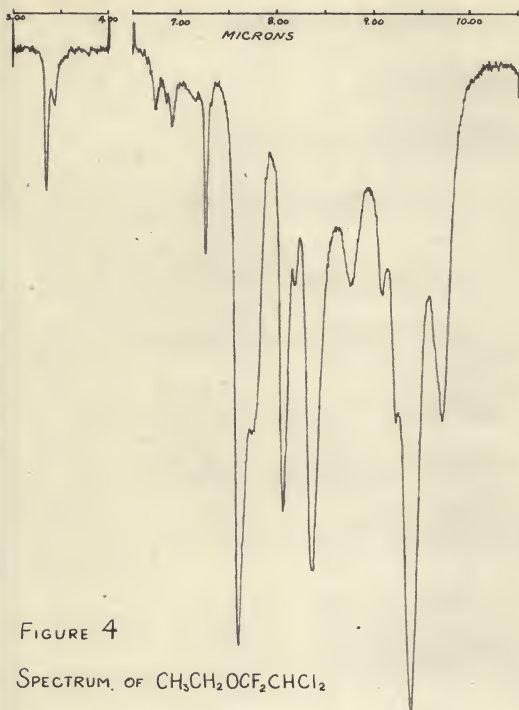
FIGURE 4

SPECTRUM. OF CH₃CH₂OCF₂CHCl₂
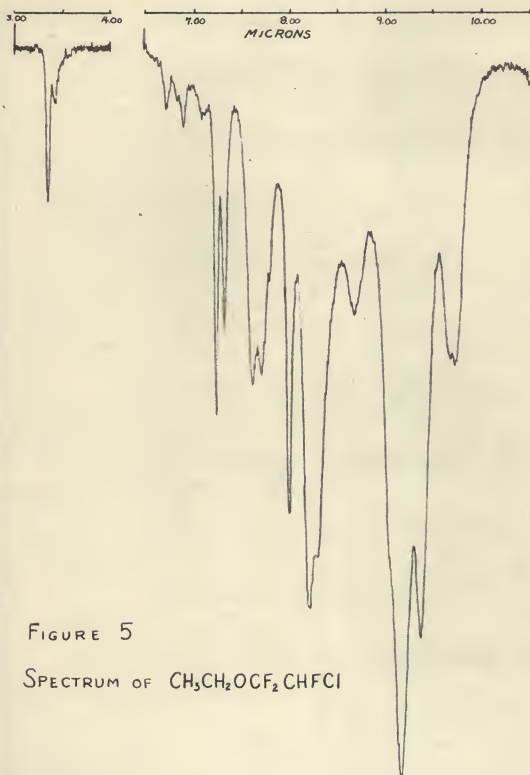
FIGURE 5

SPECTRUM OF $CH_3CH_2OCF_2CHFCl$

MICRONS
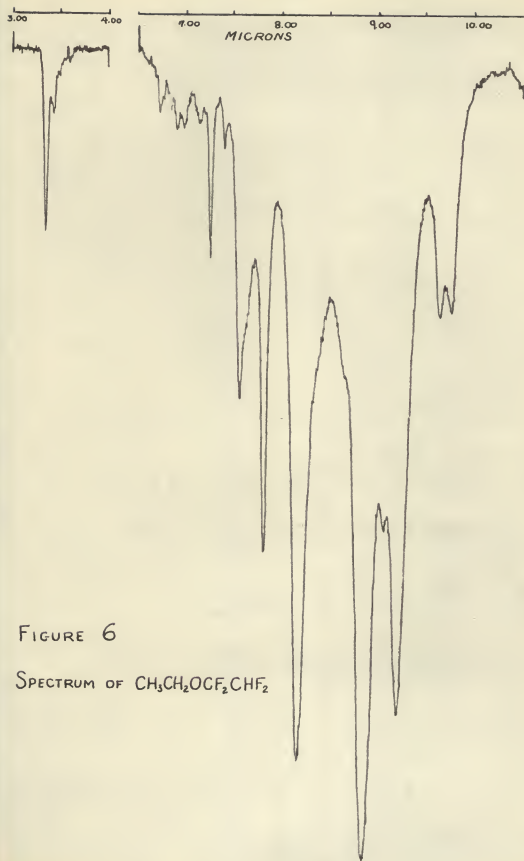
FIGURE 6

SPECTRUM OF CH₃CH₂OCF₂CHF₂
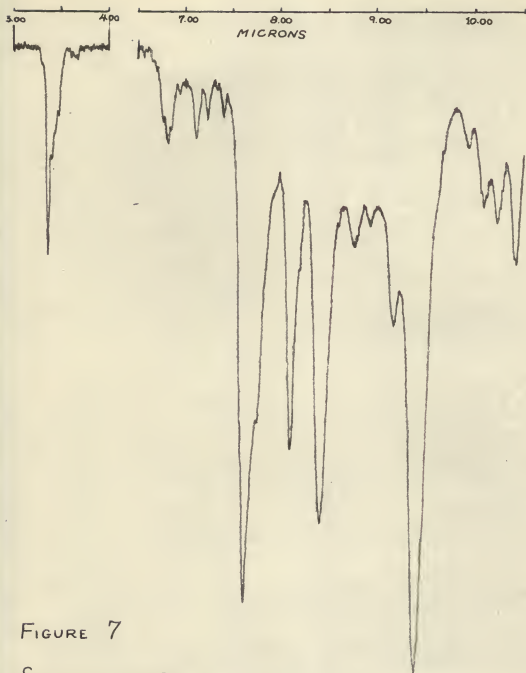
FIGURE 7

SPECTRUM OF $CH_3CH_2CH_2OCF_2CHCl_2$

FIGURE 8

SPECTRUM OF $CH_3CH_2CH_2OCF_2CHFCl$
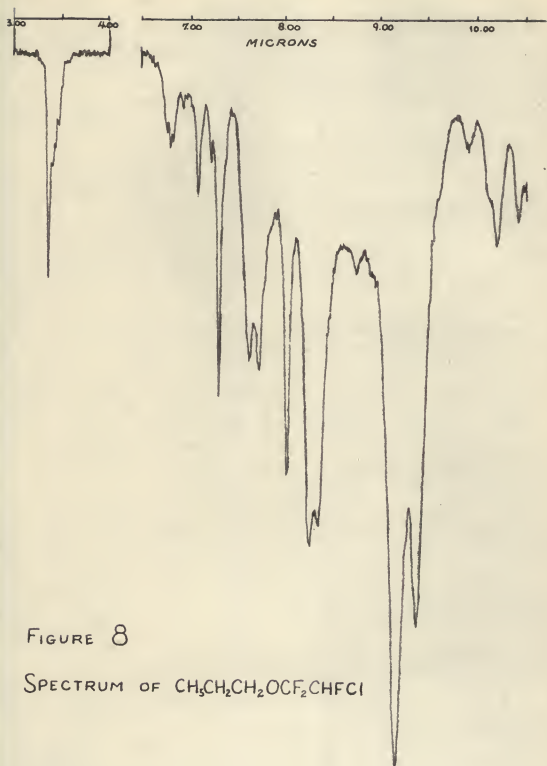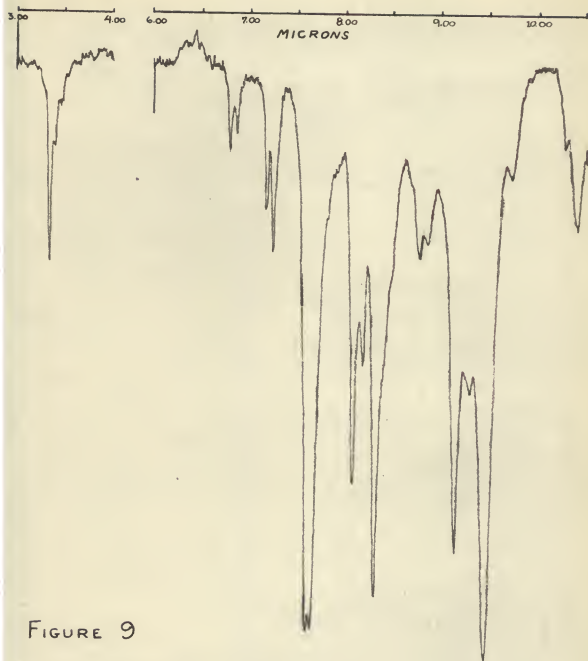
FIGURE 9

SPECTRUM OF $(CH_3)_2CHOCF_2CHCl_2$

FIGURE 10

SPECTRUM OF $(CH_3)_2CHOCF_2CHFCl$
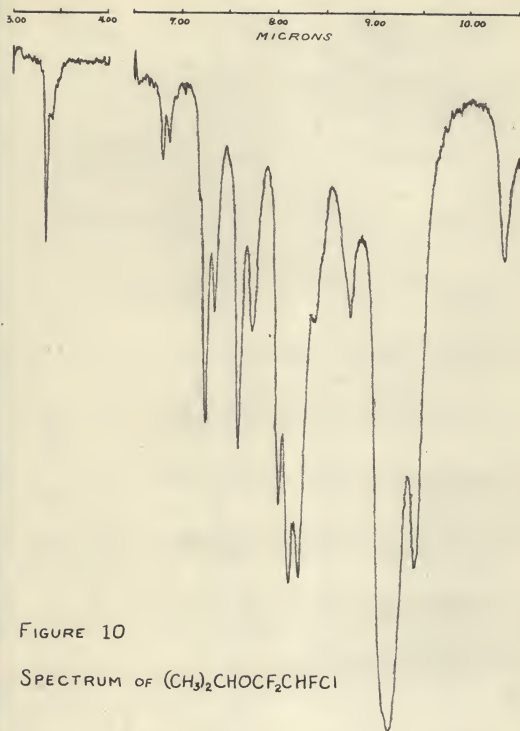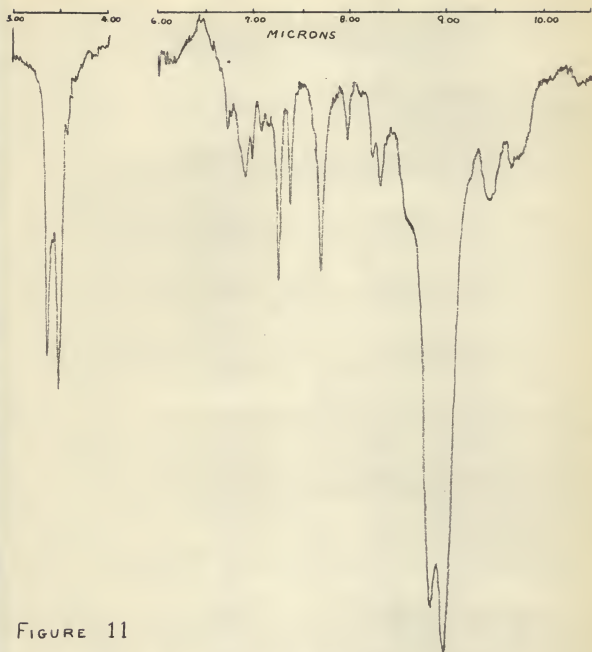
FIGURE 11

SPECTRUM OF $CH_3CH_2OCH_2CH_2Cl$
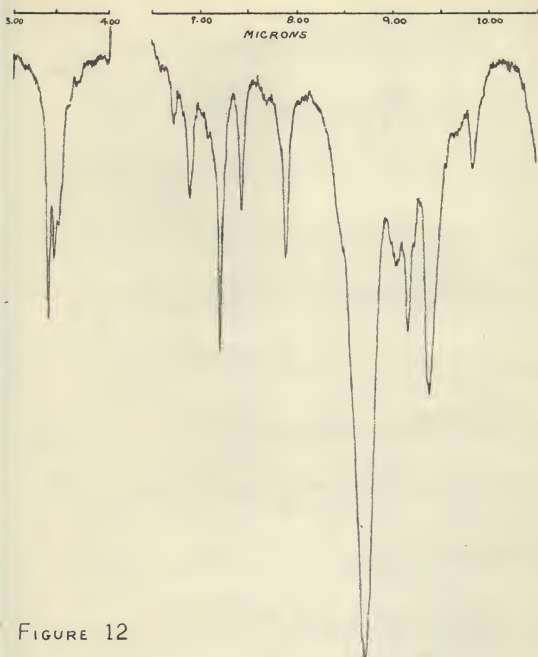
FIGURE 12

SPECTRUM OF $CH_3CH_2OCHClCH_3$

MICRONS
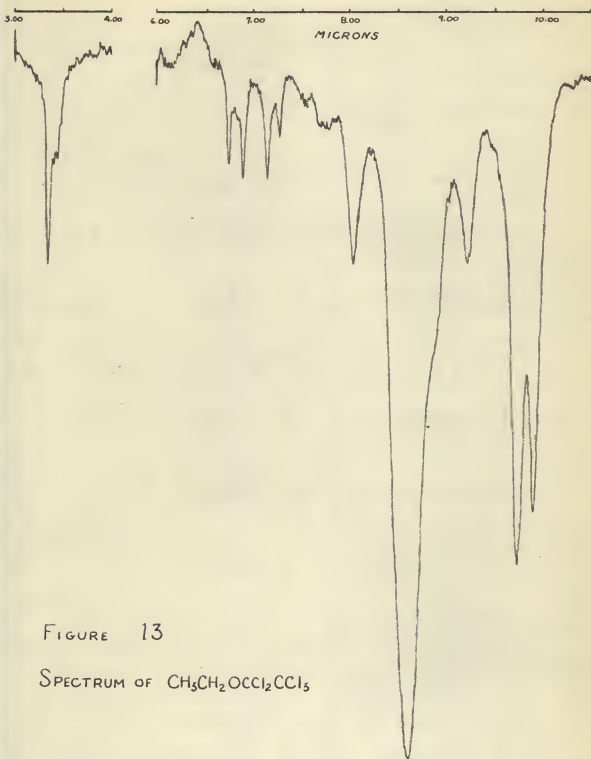
FIGURE 13

SPECTRUM OF $CH_3CH_2OCCl_2CCl_3$

CHAPTER III

DISCUSSION OF RESULTS

The Carbon-Hydrogen Stretching Region

As an aid to understanding the spectra of the substituted ethers in the C-H stretching region of the spectrum, the spectra of a few unsubstituted ethers were determined. Table I lists the absorption bands which appear in the spectra of these ethers in this region which extends from about 3.00 microns to about 4.00 microns. Also listed, for purposes of comparison, are the bands corresponding to C-H stretching vibrations in the spectra of methyl, ethyl and n-propyl alcohols. The numbers in parentheses which follow the wave length of the bands show the relative intensity of the band in its own group, the lowest numbered band being the most intense. In every case, the band of least intensity absorbs several times more weakly than the next highest one; however, the remaining bands have intensities of about the same magnitude. The infrared spectral datum for dimethyl ether which appears in the table was taken from the work of Crawford and Joyce (1).

Examination of the table shows that methyl alcohol and dimethyl ether contain a strong band between 3.42 and 3.43 microns. This band must be due to a stretching mode of the methyl group since no other C-H configuration exists in these molecules. At least it may be said that this band is characteristic of a methyl group attached to oxygen.

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TABLE I

THE SPECTRAL BANDS OF SOME UNSUBSTITUTED ETHERS AND ALCOHOLS IN THE 3.00 TO 4.00 MICRON REGION

Compound	Wave Length in Microns[*]			
Methyl Alcohol		3.42(1)	3.54(2)	
Ethyl Alcohol	3.38(1)	3.44(3)	3.48(2)	
n-Propyl Alcohol	3.39(1)	3.42(2)	3.49(3)	
Methyl Ethyl Ether	3.36(2)	3.44(3)	3.50(1)	3.55(4)
Ethyl Isopropyl Ether	3.38(1)	3.42(3)	3.49(2)	3.61(4)
Dimethyl Ether		3.43(1)		
Diethyl Ether	3.42(1)	3.47(3)	3.54(1)	3.63(4)
Diisopropyl Ether	3.37(1)	3.42(3)	3.48(2)	3.53(4)
Dibutyl Ether	3.41(1)	3.48(2)	3.58(3)	
Dihexyl Ether	3.43(1)	3.51(2)	3.58(3)	
Di-2-ethyl-hexyl Ether	3.40(2)	3.43(1)	3.55(3)	3.59(4)

[*] The numbers in parentheses after each wave length indicate the relative intensity of the band in its group. The lowest number corresponds to the most intense band.

With the introduction of a methylene group to form ethyl alcohol, a new, strong band is introduced into the spectrum at 3.38 microns; however, the bands appearing at 3.42 and 3.54 microns in the spectrum of methyl alcohol are still present in the ethyl alcohol spectrum at 3.44 and 3.48 microns. Presumably this new band is due to the methylene group adjacent to oxygen. It should also be noted that the spectrum of n-propyl alcohol contains these three bands at 3.39, 3.43 and 3.49 microns. Comparing these spectra with those of the unsymmetrical, straight-chain ethers, it appears that the leading band in the ether spectra can be identified with a methylene vibration, and that the two bands falling between 3.42 and 3.44 microns and between 3.49 and 3.50 microns are, at least in part, due to methyl stretching vibrations.

This tentative assignment contradicts the assignments made by Fox and Martin (18) in their study of hydrocarbons. These authors assign the bands occurring at 3.37 and 3.42 microns in the spectra of hydrocarbons to methyl and methylene vibrations respectively. On the basis of the structural similarity of ethers and hydrocarbons, one might argue that a correspondence between the spectra of the two classes of compounds should be found. This point of view, however, fails to consider the perturbing effect of the ether oxygen on the C-H vibrations. For this reason, a comparison with alcohols has been chosen as the most valid, particularly for the ethers of low molecular weight in which the oxygen comprises a reasonably large fraction of the molecule.

In the spectra of all the symmetrical, straight-chain ethers, a persistent and troublesome phenomenon was observed. Without exception, the spectra of these ethers possess no band in the region around 3.38 microns, the leading band of the series occurring at approximately 3.42 microns. Furthermore, this band is always one of the most intense bands in the system, even in the case of dibutyl ether and dihexyl ether. In view of these intensities it is reasonable to assign this band to a methylene vibration and to identify it with the 3.38 micron band of the unsymmetrical ethers. If this is done, the correspondence of the remaining bands in the spectra of the symmetrical ethers suggest that the whole band system has been shifted to longer wave lengths. An explanation of this behavior might be found in the symmetry of the ethers and in the duplication of groups on each side of the oxygen.

Even if the assignments set forth above are adopted, some inconsistencies still remain. In the first place, it is at once apparent that the spectrum of diisopropyl ether, which contains no methylene groups, has a strong band in the region previously ascribed to methylene vibrations. Furthermore, the relative intensities of the bands within the respective groups do not behave in the expected manner. For example, the band in the methylene region of the spectrum of ethyl isopropyl ether is the most intense band of its group, while in the spectrum of ethyl n-propyl ether it is the second most intense band, even though ethyl n-propyl ether contains a greater number of methylene groups.

Both of these anomalies would be explained if a vibration characteristic of tertiary C-H appeared in this region of the spectrum; however, no data are available which might settle this question.

Other instances occur in which the order of the band intensities seems to contradict the proposed assignment. It is not difficult to see, however, why this might be so. The ethers, although they are not very polar, do have a dipole moment, and as was pointed out in Chapter I, the intensities of absorption depend partly on the change in this dipole moment which accompanies the vibration. It then follows that the intensity of absorption due to the methyl or methylene groups in a molecule will depend on their position in the molecule as well as the number of them present. That the vibration of a methyl or methylene group far removed from the oxygen will have a different effect on the dipole moment of the molecule than will the vibration of a like group close to the oxygen seems evident.

It must be emphasized that the assignments made here are tentative and represent only the most consistent interpretation of the available data. Before more definite assignments are warranted, a detailed study using high resolution and considering many more compounds must be undertaken.

The spectra of the highly substituted ethers, with which this study is concerned, show very little similarity with those of the unsubstituted ethers. The absorption bands of these ethers in this region are

presented in Table II in the same manner as that used in presenting this data for the unsubstituted ethers in Table I. In the interests of saving space, a simple system of abbreviation has been adopted for the names of the ethers in this table. According to this system, the carbon skeleton of the substituted ethyl group and the oxygen and hydrogen attached to it have been omitted, and only the substituents and the unsubstituted alkyl group have been shown. Thus, for example, $(CH_3)_2CHOCF_2CHCl_2$ becomes $iPrF_2Cl_2$, and CH_3OCF_2CHFCl becomes MeF_2FCl. The two monochlorinated ethyl ethers appear as $EtCl(\alpha)$, for the α-substituted ether, and $EtCl(\beta)$ for the β-substituted derivative.

The table shows that the leading band in the spectra of all these ethers occurs at a slightly shorter wave length than in the spectra of the unsubstituted ethers. This behavior parallels that of the C-H vibration absorptions in the spectra of substituted hydrocarbons. For example, Herzberg (2) reports C-H absorptions at 3.28 and 3.35 microns in the spectrum of CH_2Cl_2 and at 3.29 and 3.37 microns in the spectrum of CH_3Cl. Furthermore, Nielsen, Claasen and Smith (19) assign to a methyl vibration the absorption at 3.29 and 3.36 microns in the spectrum of CH_3CF_3, and Smith and others (20) assign to a methyl vibration the absorption at 3.29 and 3.37 microns in the spectrum of CH_3CF_2Cl and the absorption at 3.31 and 3.38 microns in the spectrum of CH_3CFCl_2. These wave lengths are considerably shorter than those normally occurring in the spectra of unsubstituted, saturated

TABLE II

THE SPECTRAL BANDS OF THE SUBSTITUTED ETHERS IN THE 3.00 TO 4.00 MICRON REGION

Compound	Wave Length in Microns*			
MeF_2Cl_2	3.34(1)	3.39(3)		3.50(2)
MeF_2FCl	3.34(1)	3.39(3)		3.49(2)
EtF_2Cl_2	3.36(1)	3.43(2)		3.49(3)
EtF_2FCl	3.36(1)	3.43(2)		3.50(3)
EtF_2F_2	3.36(1)	3.44(2)		3.49(3)
$EtCl(\alpha)$	3.37(1)	3.44(2)	3.47(3)	3.57(4)
$EtCl(\beta)$	3.37(1)	3.42(3)	3.48(2)	3.56(4)
$EtCl_5$	3.37(1)	3.43(2)	3.46(2)	
$nPrF_2Cl_2$	3.37(1)	3.42(2)	3.45(3)	3.48(4)
$nPrF_2FCl$	3.37(1)	3.41(2)	3.45(3)	3.48(4)
$iPrF_2Cl_2$	3.36(1)	3.42(2)		3.48(3)
$iPrF_2FCl$	3.36(1)	3.40(2)		3.48(3)

* The numbers in parentheses after each wave length indicate the relative intensity of the band in its group. The lowest number corresponds to the most intense band.

hydrocarbons. The difference noted between the spectra of the substituted and unsubstituted ethers studied is not as large as this, presumably because the alkyl groups are partly isolated from the electronegative substituents by the oxygen.

It is interesting to note that the leading bands which occur at the shortest wave length appear in the spectra of those ethers which contain a methyl group, and that the wave length of the leading band in the spectra of the substituted ethers moves steadily toward a wave length characteristic of the unsubstituted ethers as the alkyl group becomes larger. The leading band in the spectrum of $CH_3OCF_2CHCl_2$, for example, occurs at 3.34 microns while the leading band in the spectrum of $CH_3CH_2CH_2OCF_2CHCl_2$ occurs at approximately 3.37 microns. This is, of course, to be expected, since the C-H containing groups are being moved away from the center of electronegativity and are constituting an increasingly larger part of the molecule.

Examination of the spectra shown in Figures 2 through 13 shows that the contours of the band system in the substituted ethers are quite characteristic of the alkyl group and not greatly dependent on the type of substitution as long as the amount of substitution remains constant. For example, the spectra of $CH_3CH_2OCF_2CHCl_2$, $CH_3CH_2OCF_2CHFCl$, $CH_3CH_2OCF_2CHF_2$ and $CH_3CH_2OCCl_2CCl_3$ have very similar band systems, but the spectra of $CH_3CH_2OCHClCH_3$ and $CH_3CH_2OCH_2CH_2Cl$ have bands distinctly different from these and more like those of the

unsubstituted ethers. It also appears that as the alkyl group becomes larger, the resolution of the individual bands in this region becomes poorer.

A band characteristic of a hydrogen attached to an electronegatively substituted carbon, which one might expect in the spectra of these ethers, appears to be missing. Nielsen, Liang and Smith (21) assign the absorption at 3.32 microns in the spectrum of CF_3CHCl_2 to a vibration of this type and certainly the environment of the terminal hydrogen in these ethers is similar. In the same work the bands occurring in the spectrum of CF_3CH_2Cl at 3.34 and 3.29 microns are assinged to methylene vibrations. It is quite possible that this band is not resolved in these ethers and is obscured by the relatively stronger leading band. The idea that the leading band is due to vibrations of this terminal hydrogen does not fit with the observed fact that the system of bands is characteristic of the alkyl group.

The Carbon-Hydrogen Deformation Region

The spectrum of molecules from 6.70 to 7.75 microns is characteristic of absorptions which arise from deformation vibrations of methyl and methylene groups. Some of the bands in the spectra of the substituted ethers studied can be attributed to this type of vibration; however, others can be interpreted on this basis only with difficulty. Indeed, distinctly different spectra are found for a given series of ethers which contain exactly the same alkyl group. This indicates that absorption in this region is dependent to some extent on the type and degree of substitution. Table III lists all the bands which occur in this region of the spectra of the substituted ethers studied. The same system of presentation is used as in Table II except that intensities are indicated by the letters s, strong, m, medium and w, weak. Those bands for which absorption is less than ten per cent of the incident radiation are classed as weak, those for which absorption is between ten and thirty per cent are classed as medium and those for which absorption is greater than thirty per cent are classed as strong. Bands which are underlined are shoulders, and the wave lengths given for these are approximate.

A pair of bands occurring in the ranges 6.72 - 6.75 and 6.90 - 6.94 microns appears in the spectrum of every ether which contains an ethyl group attached to the ether oxygen, and are absent in the spectra of every ether which does not possess this structure. The constant

TABLE III

THE SPECTRAL BANDS OF THE SUBSTITUTED ETHERS IN THE 6.70 TO 7.75 MICRON REGION

Compound	Wave Length in Microns*												
MeF_2Cl_2			6.87m							7.60s	7.64s		7.72s
MeF_2FCl			6.86m				7.29s				7.63s	7.67s	7.75m
EtF_2Cl_2	6.73w		6.90w				7.26m				7.63s		7.75m
EtF_2FCl	6.74w			6.92w			7.26s	7.34s			7.64s		7.73s
EtF_2F_2	6.74w			6.92w	6.99w	7.17w	7.27m	7.41m		7.57s	7.64m		
$EtCl(\alpha)$	6.75w			6.92w			7.24m	7.46w					
$EtCl(\beta)$	6.72w			6.92m	6.97m		7.25m	7.37w				7.70m	
$EtCl_5$	6.77w			6.92w		7.18w	7.28w						
$nPrF_2Cl_2$		6.83m			6.97w	7.13m	7.23m	7.40w			7.63s		7.75s
$nPrF_2FCl$		6.81w				7.10m	7.24w	7.32s			7.64m		7.74m
$iPrF_2Cl_2$		6.80w	6.87w			7.18w	7.25m				7.63s	7.67s	
$iPrF_2FCl$		6.80m	6.87m				7.25s	7.35s		7.60s	7.63s		7.74m

*The letters w, m and s which follow the wave length indicate the intensity of the band and stand for weak, medium and strong intensity respectively.

nature of these bands and their close dependence on this structure
seems to indicate that they are associated with two modes of deformation
of some part of the ethyl structure. The possibility that these two bands
originate from a methyl deformation cannot be excluded; however, their
absence in the spectra of the substituted n-propyl and isopropyl ethers
studied tends to eliminate this as a possible assignment. It would ap-
pear, in the light of available data, that this absorption is due to the
deformation of a methylene group in the oxygen-linked ethyl group.

The spectra of $CH_3CH_2CH_2OCF_2CHFCl$ and
$CH_3CH_2CH_2OCF_2CHCl_2$ do not contain this band, but show, instead, a
band at 6.81 and 6.83 microns respectively. The corresponding iso-
propyl ethers both have a band in their spectra at 6.80 microns. Al-
though these bands appear to be characteristic of the alkyl group, no
unambiguous assignment is possible. They may be due to methyl or
methylene deformations.

Reference to Table III shows that four of the substituted ethers
studied exhibit a band at either 6.86 or 6.87 microns in their spectra.
The lack of similarity in structure of these ethers seems to indicate
that this band does not originate with a vibration common to all the
molecules, but, rather, from different vibrations which happen to have
the same energy. In the methyl ethers this band must correspond to a
methyl deformation, but assignment in the case of the isopropyl ethers
is not possible from available data.

Another interesting system of bands occurs between 7.18 and 7.37 microns in the spectra of the substituted ethers. It is this region which contains the very characteristic band associated with the deformation of a methyl group attached to a carbon atom. Hastings and others (22) have pointed out that, in hydrocarbons, a methyl group attached to a methylene group absorbs consistently at 7.25 microns. McMurray and Thornton (23) report that absorption between 7.23 and 7.26 microns characterizes this structure. They further state that the presence of two methyl groups on the same carbon causes this band to split into two components which fall between 7.20 and 7.24 microns and 7.29 and 7.31 microns respectively.

Examination of Table III shows that the spectra of every ether in which a single methyl group is attached to a carbon atom contains this band between 7.23 and 7.28 microns while the spectrum of $CH_3OCF_2CHCl_2$ contains no band at all in this region. The spectrum of CH_3OCF_2CHFCl, however, does contain a band at 7.29 microns; a band much stronger than the ones occurring in the spectra of the ethers containing the methyl-on-carbon structure. Furthermore, it appears that the $ROCF_2CHFCl$ ethers which do have this methyl-on-carbon structure possess two bands in this region of the spectrum; one in the region from 7.24 to 7.26 microns and the other between 7.32 and 7.35 microns. The only ether of the type $ROCF_2CHCl_2$ which possesses two bands in this region is the isopropyl ether; however, the band at 7.40

microns in the spectra of this compound is weak and can probably be attributed to a methyl or methylene vibration.

Since this behavior is consistent and so closely allied with the structure of the ethers, some explanation should be found in the examination of these structures. One such interpretation is available if one assumes that the 7.29 micron band in the spectrum of CH_3OCF_2CHFCl originates in the deformation of the C-H bond in the CHFCl group. The presence of this band in the spectra of the other $ROCF_2CHFCl$ ethers between 7.32 and 7.35 microns may be attributed to the same source, the shift in wave length having been caused by Fermi Resonance with the vibration associated with the methyl group in the methyl-on-carbon structure which occurs between 7.24 and 7.26 microns in the spectra of these compounds. The absence of this band in the spectra of the rest of the ethers, particularly that of CH_3OCF_2CHFCl, may be explained by assuming that the higher symmetry of these ethers acts in such a way as to make this C-H vibration infrared inactive.

It is difficult to understand how this situation might come about. The ethers in question have the possibility of only a very low symmetry, and this symmetry depends on the various groups appearing in very precise equilibrium positions. Although this is possible, it seems likely that the ethers exhibit a more compact and less symmetrical structure. Measurement of the dipole moments of these ethers as well as a study of their Kerr constants should give pertinent information.

An alternate explanation for the observed bands is possible which does not involve considerations of the molecular symmetry. In this scheme the 7.29 micron band in the spectrum of CH_3OCF_2CHFCl is assigned to a stretching vibration of the C-F bond in the CHFCl group. The observed bands are equally well explained by this assumption, and the high intensity of the band tends to confirm this view. The band which occurs between 7.23 and 7.27 microns in the spectra of compounds containing the methyl-on-carbon structure is then assigned, as before, to deformations of the methyl group in this structure. The spectra of compounds in which both groups appear contain both bands; however, the band associated with the CHFCl structure has been shifted to longer wave lengths by resonance.

Unfortunately, this latter view is not entirely without defects. Nielsen, Smith and others (19-21) (24-26) have conducted an extensive series of studies of the spectra of halogenated ethanes. In this study, they did not find absorption at so short a wave length which could be attributed to C-F stretching unless CF_3 groups were present or unless the compounds were unsaturated. No compounds were examined in these studies which possessed carbon atoms with exactly the same substituents as the compounds treated in the present work, and comparison is rather difficult for this reason. The spectra of CH_3CH_2F (26), CF_3CFCl_2 (24), CCl_3CFCl_2 (25), and CH_3CFCl_2 (20), all of which contain a carbon atom with a single fluorine substituent in conjunction with varying numbers

of chlorine and hydrogen atoms, were studied, however. In these spec-
tra bands due to the isolated fluorine are assigned at no shorter wave
lengths than 8.54, 9.07, 9.08, and 9.12 microns for the respective
ethanes.

This evidence notwithstanding, the latter explanation of these
bands seems the more tenable since there is some evidence, to be dis-
cussed later, which indicates that the ether oxygen may have the effect
of moving C-F bands to shorter wave lengths. The evidence is, how-
ever, not as conclusive as might be desired, and in order for a definite
decision to be reached, the Raman spectra of the ethers should be in-
vestigated. A study of these spectra should eliminate or confirm the
first alternative suggested.

A further comparison of the spectra of the compounds included
in this study illustrates a striking and characteristic difference between
the spectra of those compounds containing fluorine as a substituent and
those containing only chlorine. While the spectra of the chlorinated
ethers have only medium bands in the region from 7.50 to 7.75 microns,
the ethers containing fluorine, without exception, possess a system of
two or three strong spectral bands in this region. These facts indicate
clearly that this system of bands must be associated with the CF_2 group
which is present in all of the fluorinated ethers.

The group contains several partially resolved bands which may
represent rotational splitting of a single vibration band. If this view is

adopted, it explains the partial dependence of the contours of the band system on the alkyl group present, and the greater dependence of these contours on the type of halogen substitution. Furthermore, construction of Herschfelder models of these molecules show several possibilities for interaction between the fluorine atoms and the hydrogens of the alkyl group. If this interaction occurs, it would depend, of course, on the shape of the alkyl group, and modification of the spectra would be expected.

The presence of absorption due to CF_2 groups at so short a wave length is somewhat surprising in light of the studies of Nielsen and Smith; however, the presence of oxygen in the ether molecule seems to have the same effect as unsaturation, which moves the absorption due to CF_2 to shorter wave lengths. For example, Smith, Nielsen and others (20) assign an absorption at 8.12 microns to a CF_2 stretching vibration in the spectrum of CH_3CF_2Cl, but in the spectrum of $CF_2=CF_2$, studied by Smith, Nielsen and Classen (27), the highest occurring CF vibration is assigned at 7.68 microns.

The Region Between 7.75 and 10.00 Microns

This region of the spectrum of an organic molecule contains infrared absorption bands associated with C-C stretching vibrations, C-O stretching vibrations and the rocking vibrations of methyl and methylene groups (5). When fluorine is present in the molecule, the C-F vibrations also give rise to absorption bands in this region (5) (2). The large number of different structures which cause absorption in this region make interpretation very difficult, not only because of the plurality of the bands but also because the respective bands do not retain their individuality. This loss of individuality comes about through the similarity of the atomic masses and force constants of the structures which cause these absorptions.

The spectra of the ethers with which this study is concerned would be expected to exhibit bands associated with C-F, C-O and C-C vibrations as well as rocking vibrations of methyl or methylene groups. The bands of these compounds are listed in Table IV in the same manner used to present similar data previously. For convenience, the bands which seem to retain their identity throughout the series of compounds have been arranged in columns which have been numbered. This procedure seems justified for the fluorine-containing ethers since the rather constant wave length and similar appearance of most of the bands make their identification with each other easy; however, some discrepancies exist. In general, when any doubt existed as to identity, the

band was placed in a separate column. It should be further noted that the table does not imply that any relation exists between the bands in the spectra of the fluorine-containing ethers and the bands in the spectra of those containing only chlorine even though these correlations may exist in certain cases. The data for the ethers containing only chlorine were presented for the sake of comparison and were fitted into the table in the most convenient fashion.

The spectra of the $ROCF_2CHCl_2$ ethers exhibit six bands, numbered 1, 2, 3, 5, 7 and 9, which retain their identity very well as the alkyl group is changed. In addition, the first four bands exhibit, qualitatively, a regular behavior with regard to the shift in wave length which accompanies a change in the alkyl group. In each case, the bands occur at the shortest wave length in the methyl ether spectrum, are moved to longer wave lengths in the ethyl ether spectrum, remain the same or increase in wave length in the spectrum of the n-propyl ether but shift to shorter wave lengths in the spectrum of the isopropyl ether. This effect is particularly large in the band numbered 3 in the table.

The intensity of these bands, their position in the spectra, and the small magnitude of the shift which occurs when the alkyl group is changed, indicate that they are associated with vibrations of the substituted part of the molecules rather than with vibrations of the unsubstituted alkyl group. If this is the case, the observed shift must be explained by the fact that the alkyl groups, operating through the ether oxygen,

TABLE IV

THE SPECTRAL BANDS OF THE SUBSTITUTED ETHERS IN THE 7.75 TO 10.0 MICRON REGION

Compound	Wave Length in Microns*										
	1	2	3	4	5	6	7	8	9	10	11
MeF_2Cl_2	8.05s	8.18s	8.27s				9.15m		9.37s	9.77m	9.98m
EtF_2Cl_2	8.07s	8.20s	8.37s		8.77m		9.09m	9.25m	9.41s	9.72m	
$nPrF_2Cl_2$	8.12s	8.20m	8.43s		8.77m	8.94m	9.18m		9.42s		9.93w
$iPrF_2Cl_2$	8.09s	8.18m	8.32s	8.41m	8.76m	8.85m	9.14s	9.29m	9.47s	9.73m	
MeF_2FCl	7.99s	8.14s			8.63s	9.00s	9.15s		9.34s	9.73m	9.98m
EtF_2FCl	8.02s	8.23s	8.32s		8.69m	9.05s	9.18s		9.38s	9.72m	
$nPrF_2FCl$	8.03s	8.27s	8.36s		8.75m		9.17s		9.37s		9.91w
$iPrF_2FCl$	8.02s	8.14s	8.23s	8.40m	8.76m	9.05s	9.18s		9.45s		
EtF_2F_2	7.84s	8.20s			8.70m		8.88s	9.09s	9.22s	9.66m	9.77m
$EtCl(\beta)$	7.97w		8.23w		8.85s	8.97s			9.43m	9.70m	
$EtCl(\alpha)$	7.92m		8.32m		8.76s	9.07m	9.19m		9.41m		9.87w
$EtCl_5$	8.07m				8.65s	9.26m				9.78s	9.95s

* The letters w, m and s which follow the wave lengths indicate the intensity of the band and stand for weak, medium and strong intensity respectively.

have some effect on the vibrations characteristic of the substituted part of the molecules. The difference in the electron-releasing power of the alkyl group is probably the effect which operates here; however, the shifts in wave length observed are not entirely consistent with an explanation on this basis.

Ordinarily isopropyl groups are considered more electron-releasing than ethyl groups which are, in turn, more electron-releasing than methyl groups; the position of n-propyl groups should be somewhere between that of ethyl and that of isopropyl groups in this series (28). If the isopropyl groups are not considered, the continued shift to longer wave lengths in the series methyl, ethyl, n-propyl is entirely consistent with the postulate that electrons are being made more available in the bonds of the substituted portion of the molecules. This availability of electrons would then have the effect of slightly decreasing the force constant of these bonds. The failure of the isopropyl ether to fall in the expected position may be due to the bulky character of the isopropyl group which causes a distortion of the C-O-C bonds.

The bands numbered 7 and 9 in Table IV do not exhibit this regular shift in wave length, but are very characteristic of the spectra of both types of substituted ethers. There is some evidence to indicate that these are associated with vibrations of the CF_2 group which occurs in both ether structures. Letaw and Gropp (29) observed similar bands in the spectra of CHF_2CONH_2, and Smith and others (20) report bands

at 8.12, 8.32, 8.87 and 9.07 microns in the spectrum of CH_3CF_2Cl which they ascribe to this structure.

In general, it is impossible to make absolute assignments for some of the bands which occur in this region. Most of the persistent bands seem to be associated with the substituted part of the molecule, although the band numbered 5 in the table may be due to a methyl rock occurring in the unsubstituted alkyl group.

The spectra of the $ROCF_2CHFCl$ ethers are not as consistent as those of the ethers discussed above. Some of the bands which appear in the spectra of the $ROCF_2CHCl_2$ ethers are easily identified in the spectra of the $ROCF_2CHFCl$ ethers. Those are the bands numbered 1, 5, 7 and 9 in Table IV. It will be noted that these bands follow the same pattern of wave length shift as do the corresponding bands in the $ROCF_2CHFCl$ ethers. These are the bands numbered 1, 5, 7 and 9 in Table IV. It will be noted that these bands follow the same pattern of wave length shift as do the corresponding bands in the $ROCF_2CHCl_2$ ether spectra except that the wave length is somewhat shorter in each case. This shift to shorter wave lengths is probably due to the additional fluorine atom present, an effect which has been observed before (26).

The failure of the band numbered 3 in the table to appear in the spectrum of CH_3OCF_2CHFCl is unexpected; however, examination of spectrum of this compound shows that the band at 8.14 microns is quite broad enough to mask a band of lower intensity occurring, for

example, at 8.25 microns.

The spectrum of $CH_3CH_2OCF_2CHF_2$ is quite similar to the spectra of the other two ethyl ethers except that there seem to be some missing bands. Before any conclusions are drawn from this spectrum it is essential that the spectra of other members of this series be observed; however, it is interesting to notice that the wave length of the band numbered 1 in the table has been decreased by the additional fluorine present, an effect which has been observed previously (26).

The problem of the location of the absorption band associated with the C-O stretching vibration is of paramount importance. That the absorption associated with this vibration occurs somewhere in this region is beyond doubt; however, its location is difficult to determine due to the interfering absorptions which are present. Park and others (12), in a study of the infrared spectra of the $ROCF_2CHCl_2$ ethers, assign the absorption occurring between 9.00 and 9.50 microns to this structure; however, this assignment does not seem correct in view of evidence obtained in this study.

In order to resolve this inconsistency, the spectra of several unsubstituted ethers were first determined, and the band which seemed to correspond to the C-O stretching vibration was selected. In general, this band is not difficult to select since it is the strongest band in this region of the spectra of unsubstituted ethers; however, the ethers which contained isopropyl groups possessed several bands of about equal

intensity in this region of the spectrum. These ethers are not considered
in the discussion which is to follow because the band associated with the
C-O stretching vibration could not be selected with certainty. Further-
more, the data obtained from the ether spectra in which the band could
be unequivocably assigned seem sufficient to illustrate the behavior of
unsubstituted ethers. Table V lists the position of this band in the spec-
tra of n-propyl ethyl ether, diethyl ether, methyl ethyl ether and di-
methyl ether. The datum for dimethyl ether was obtained from the work
of Crawford and Joyce (1).

        The next step in the resolution of this problem was the deter-
mination of the spectra of α-chloro-ethyl ethyl ether, β-chloro-ethyl
ethyl ether and pentachloro-ethyl ethyl ether in order to find the effect
of electronegative substitution on the wave length of the C-O band.
The results of this experiment are also listed in Table V.

        The band in question is extremely easy to identify in the spec-
tra of α-chloro-ethyl ethyl ether and pentachloro-ethyl ethyl ether
because of its large intensity and because of the fact that no interfering
bands occur in this region. Two bands, however, appear in the spec-
trum of β-chloro-ethyl ethyl ether, and both are shown in the table.
It is clear that either of these two bands illustrates the wave length
shift equally well so that a decision as to which band should be assigned
to the C-O vibration does not need to be made. It is also possible that
both bonds belong to the C-O vibration and are the result of splitting.

TABLE V

THE SPECTRAL BAND ASSOCIATED WITH THE CARBON-OXYGEN STRETCHING VIBRATION IN VARIOUS ETHERS

Compound	Wave Length in Microns
n-Propyl Ethyl Ether	8.94
Diethyl Ether	8.95
Methyl Ethyl Ether	8.93
Dimethyl Ether	8.91
β-Chloro-ethyl Ethyl Ether	8.85 -- 8.97
α-Chloro-ethyl Ethyl Ether	8.76
Pentachloro-ethyl Ethyl Ether	8.65

The data listed in Table V reveal that the unsubstituted ethers absorb, in each case, at a wave length greater than 8.90 microns, the lowest wave length of absorption occurring in the spectrum of dimethyl ether at 8.91 microns. When an electronegative chlorine atom is introduced, as in β-chloro-ethyl ethyl ether, the absorption either remains at much the same wave length or is shifted to a considerably lower one, depending on the band which is chosen. Either choice can be justified, but on the basis of the evidence contributed by the spectra of the remaining ethers in this group, the choice of the shorter wave length seems more logical.

The position of the band in the spectra of α-chloro-ethyl ethyl ether at 8.76 microns and of pentachloro-ethyl ether at 8.65 microns clearly shows the tendency of the band in question to shift to shorter wave lengths when electronegative substituents are present on one of the alkyl groups. The data also show that the magnitude of the shift is greater when the chlorine is closer to the C-O bond and still greater when the number of electronegative substituents is increased.

In view of these facts, the spectra of the ethers containing fluorine would not be expected to show absorption associated with the C-O stretching vibration in the region in which it occurs in the unsubstituted ethers. On the contrary, the presence of the two highly electronegative fluorine atoms adjacent to the C-O bond should tend to move the absorption to even shorter wave lengths than were encountered in the

chlorinated ethers. Reference to Table IV shows that there is just one
band in the spectra of the ethers which fulfils the necessary conditions.
This band is numbered 3 in Table IV. It is also interesting to note that
this band is the most sensitive to the alkyl group of the ether. This fits
well with the postulate that this band is associated with the C-O stretch-
ing vibration since this structure is adjacent to the alkyl group.

For the reasons set forth above, it seems likely that this band
is due to the vibrations of the ether linkage, and that the shift has been
caused by an increase in force constant of this linkage through the agency
of the electronegative fluorine and chlorine atoms.

CHAPTER IV

SUMMARY

In this study the infrared spectra of two series of fluorine-containing ethers were examined in the region between 2.00 and 10.00 microns. The ethers of both these series are of the same general type, having an unsubstituted alkyl group on one side of the oxygen and a substituted ethyl group on the other side. The general formulas for these series are $ROCF_2CHCl_2$ and $ROCF_2CHFCl$, the R representing an unsubstituted alkyl group. The alkyl groups considered in this study were methyl, ethyl, n-propyl and isopropyl for each series. The spectrum of $CH_3CH_2OCF_2CHF_2$ was also determined and studied.

The spectra of several unsubstituted ethers as well as the spectra of α-chloro-ethyl ethyl ether, β-chloro-ethyl ethyl ether and pentachloro-ethyl ethyl ether were also determined for purposes of comparison.

A study of the C-H stretching absorptions (3.00 - 4.00 microns) in the spectra of a few symmetrical and unsymmetrical, unsubstituted ethers was made, and some very tentative assignments were arrived at on the basis of available data. This study was made in the hope that it would be valuable in interpreting the spectral bands of the substituted ethers in this region; however, little basis for comparison was found.

The presence of fluorine in the molecule was found to diminish

the wave length at which these vibrations cause absorption, the effect
being most pronounced in the spectra of the substituted methyl ethers.
As the unsubstituted alkyl group increases in size, the wave length of
the leading band in the spectra of the substituted ethers approaches that
observed in the spectra of the unsubstituted ethers, but the resolution of
the individual bands becomes poorer. It was further noted that the
contours of this band system in the substituted ethers are quite typical
of the unsubstituted group present and independent of differences in the
fluorine substitution.

No band was positively identified which might be associated
with the stretching vibration of the C-H bond in the substituted part of
the molecules. Apparently this absorption is quite weak or is effectively
masked by other bands which occur in this region.

The spectra of the fluorine-substituted ethers contain several
bands in the region between 6.70 and 7.75 microns, which are associated
with deformation vibrations of methyl or methylene groups. A pair of
bands characteristic of a methylene group located between a methyl
group and an oxygen were identified in the spectra of substituted ethers
containing this structure. These bands correspond to the two modes of
deformation, one occurring between 6.72 and 6.75 microns and the other
between 6.90 and 6.94 microns. The spectra of the substituted methyl
ethers contain a band between 6.86 and 6.87 microns which corresponds
to a deformation vibration of the methyl group.

A band, missing in the spectrum of $CH_3OCF_2CHCl_2$ but found in the spectra of the other ethers of this series between 7.23 and 7.28 microns, was attributed to a deformation vibration of a methyl group attached to carbon. In the spectra of $CH_3CH_2OCF_2CHFCl$, $CH_3CH_2CH_2OCF_2CHFCl$ and $(CH_3)_2CHOCF_2CHFCl$, however, an additional band was found between 7.32 and 7.35 microns. The presence of this band and the appearance of a band at 7.29 microns in the spectrum of CH_3OCF_2CHFCl was attributed to an absorption associated with the stretching vibration of the C-F bond in the CHFCl group. The possibility that this band was due to a deformation vibration of the C-H bond in the substituted part of the molecules and did not appear in the spectra of the $ROCF_2CHCl_2$ ethers on account of the symmetry of the molecules was considered; however, the observed intensity of the band and the rather stringent symmetry conditions which must be met if this explanation is to be valid militate against the acceptance of this view.

A group of strong bands between 7.50 and 7.75 microns in the spectra of all the ethers containing fluorine was attributed to stretching vibrations of the C-F bonds in the CF_2 group. This assignment was made on the basis of comparisons of the spectra of the ethers containing fluorine with those of ethers containing only chlorine as a substituent. Although these bands change slightly in shape as the unsubstituted alkyl group of the ether is changed, the wave lengths of the intensity maxima remain fairly constant, an observation which lends strength to the

interpretation adopted.

The difficulty of assigning the bands which occur between 8.00 and 10.00 microns has been discussed; however, the similarities which exist in the spectra of the ethers containing fluorine led to the conclusion that these bands were associated with the substituted part of the molecules rather than with the unsubstituted alkyl group. This being the case, the bands must be due to stretching vibrations of the C-F bonds, the stretching vibrations of the C-C bond, or the stretching vibration of the C-O bond.

Four of the observed bands in the spectra of the $ROCF_2CHCl_2$ and $ROCF_2CHFCl$ ethers were observed to exhibit a systematic shift in wave length which, although small, can be correlated with the alkyl group present in the ether molecule. It was observed that alkyl groups with greater electron-releasing power shifted these bands to slightly longer wave lengths. This shift was attributed to a decrease in the force constant in the vibrating bond caused by the greater availability of electrons. Isopropyl groups proved an exception to this tendency, and it was postulated that this was due to steric factors which interfered with the efficiency of electron release.

A system of bands found in the spectra of the fluorine-containing ethers between 9.00 and 9.50 microns was attributed, by inference, to vibrations associated with the CF_2 group. This interpretation was adopted because of the typically high intensity of these absorptions and

since absorption in this region is characteristic of several compounds which contain this group.

A general tendency of bands in this region of the spectra of the $ROCF_2CHCl_2$ ethers to move to shorter wave lengths in the spectra of the $ROCF_2CHFCl$ ethers was noted, and, furthermore, a continuance of this trend was observed in the spectrum of $CH_3CH_2OCF_2CHF_2$. This phenomenon was attributed to the presence of additional fluorine in the molecule.

The attempt to determine the absorption characteristic of the C-O stretching vibration in the spectra of the fluorine-containing ethers met with success. It was discovered, by comparing the spectra of the unsubstituted ethers with the spectra of α-chloro-ethyl ethyl ether, β-chloro-ethyl ethyl ether and pentachloro-ethyl ethyl ether, that the presence of an electronegative substituent in the ether molecule causes this vibration to move to shorter wave lengths. It was further noted that the magnitude of this shift depends on the distance between the C-O bond and the electronegative atom as well as the number of electronegative substituents present.

When the spectra of the fluorine-containing ethers were considered, it was apparent that the same effect must operate to an even greater extent. The amount of electronegative substitution is great, and the fluorine atoms present are even more electronegative than chlorine. These facts led to the selection of an absorption band falling

between 8.20 and 8.43 microns in the spectra of the various ethers as the one characteristic of the C-O vibration of these molecules. The relatively large dependence of the wave length of this band on the unsubstitued alkyl group present confirmed this selection.

In conclusion, it may appear that this study has posed more questions than it has answered; however, new information of a general nature has been uncovered. The postulate that the presence of fluorine in a molecule tends to increase the energy of bond vibration has been confirmed, and good evidence has been advanced that the C-O bond vibration is particularly sensitive to this effect. It has been shown that the wave length at which a particular vibration occurs can be correlated with the inductive properties of the various other atoms and groups present in the molecule. The further exploration of this fact may be of value in the interpretation of the spectra of unknown compounds.

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BIOGRAPHICAL NOTE

Earl Wells McKisson was born on December 24, 1925, in Clearwater, Florida, and received his early education in the public schools of Pennsylvania and Florida. He graduated from Clearwater High School, Clearwater, Florida in June, 1943.

He matriculated at North Carolina State College of Agriculture and Engineering in August, 1943, as a member of the Army Specialized Training Program, and remained there until called to active duty in February, 1944. He served in the army until April, 1946, when he was honorably discharged.

In September, 1946, he entered the University of Florida, receiving from this institution the degree, Bachelor of Science in Chemistry, with honors, in June, 1949, and the degree, Master of Science, in June, 1951. While a graduate student, he was employed as a Graduate Assistant and, later, as a Teaching Assistant in the Department of Chemistry. In June, 1952, he was awarded a National Science Foundation Predoctoral Fellowship, and in June, 1953, this fellowship was renewed for an additional year.

While attending college, he was elected to Gamma Sigma Epsilon, Delta Phi Alpha and Phi Kappa Phi. He is a member of the American Chemical Society.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

January 29, 1953

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